

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

F3

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C07C 59/305, 51/27</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 94/14745</b> <b>(43) International Publication Date:</b> 7 July 1994 (07.07.94)
<b>(21) International Application Number:</b> PCT/EP93/03693 <b>(22) International Filing Date:</b> 22 December 1993 (22.12.93) <b>(30) Priority Data:</b> 07/996,268 24 December 1992 (24.12.92) US	<b>(81) Designated States:</b> AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>	
<b>(71) Applicant (for CA only):</b> SHELL CANADA LIMITED [CA/CA]; 400 4th Avenue S.W., Calgary, Alberta T2P 2H5 (CA). <b>(71) Applicant (for all designated States except CA):</b> SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). <b>(72) Inventor:</b> FRIED, Herbert, Elliott, 11634 Highgrove Drive, Houston, TX 77077 (US).		
<b>(54) Title:</b> PREPARATION OF POLYOXYALKYLENE-ALPHA,OMEGA-DICARBOXYLIC ACIDS  <b>(57) Abstract</b>  A process for the preparation of a polyoxyalkylene-alpha,omega-dicarboxylic acid by reacting the corresponding polyoxyalkylene glycol with a stable free radical nitroxide in the presence of a NO <sub>x</sub> -generating compound and optionally, an oxidant and/or a solvent, at a temperature in the range of from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha,omega-dicarboxylic acid.		

*FOR THE PURPOSES OF INFORMATION ONLY*

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## PREPARATION OF POLYOXYALKYLENE-ALPHA, OMEGA-DICARBOXYLIC ACIDS

This invention relates to a process for the preparation of polyoxyalkylene-alpha,omega-dicarboxylic acids by the oxidation of the corresponding polyoxyalkylene glycols in the presence of a stable free radical nitroxide and a  $\text{NO}_x$ -generating compound.

5 Dicarboxylic acids are useful as chelating agents, detergent builders, and emulsifying agents. These acids, being composed of only the elements C, H and O, do not pose the environmental problems that other compounds containing heteroatoms such as N, S, and P pose. The alpha,omega- dicarboxylic acids can be prepared in  
10 a two-step process by first reacting a glycol with ethylene oxide and an alkaline catalyst and thereafter converting the polyoxy-alkylene glycol to a polyoxyalkylene-alpha,omega-dicarboxylic acid.

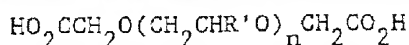
It is known from US patents Nos. 5,162,579; 5,166,422; 5,166,423; 5,179,218; 5,175,359; and 5,175,360 to use a stable free  
15 radical nitroxyl and a  $\text{NO}_x$ -generating compound (e.g., nitrous acid, nitric acid, nitrosodisulphonate, etc.) and/or a chlorine-containing oxidant (chlorine, hypochlorite) in the preparation of alkoxy-alkanoic acids from the corresponding alkoxyalkanols. Although yield and selectivity in the disclosed processes are high, in  
20 addition to the desired alkoxyalkanoic acids, also esters; formates; and (due to cleavage of the ether group) fatty acids have been found. Such processes would therefore appear not suitable for selective conversion of polyoxyalkylene glycols into the corresponding polyoxyalkylene-alpha,omega-dicarboxylic acids, as one would  
25 expect by-product formation comprising (cyclic) esters (due to the presence of both a carboxyl group and a hydroxyl group on the same molecule) and polyoxyalkylene-alpha-hydroxy-omega-carboxylic acids.

One would expect this problem to aggravate in case of only part of the polyoxyalkylene glycols is converted (for instance at  
30 starvation conditions, etc.).

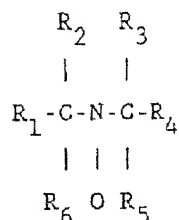
- 2 -

It has now surprisingly been found that polyoxyalkylene-alpha,omega-dicarboxylic acids can be produced in high yields and with high selectivities by using a stable free radical nitroxide and a  $\text{NO}_x$ -generating compound and optionally, an oxidant and/or a solvent.

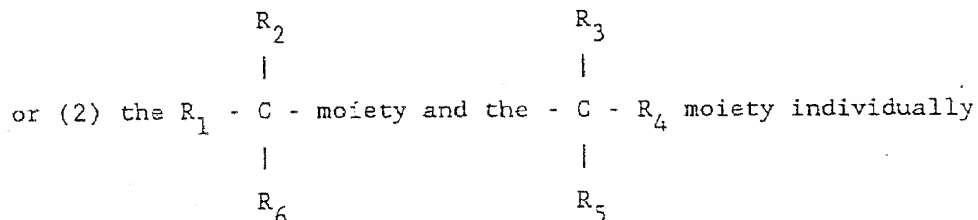
This invention relates to a process for the preparation of a polyoxyalkylene-alpha,omega-dicarboxylic acid of the formula:



wherein  $\text{R}'$  is hydrogen or methyl or mixtures thereof (on the individual molecule) and  $n$  is an integer of from 0 to 5,000 which comprises reacting the corresponding polyoxyalkylene glycol with a stable free radical nitroxide having the formula:



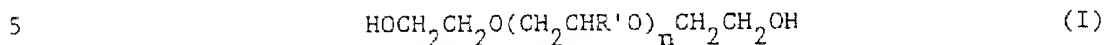
wherein (1) (a) each of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  and  $\text{R}_4$  is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms, and (b)  $\text{R}_5$  and  $\text{R}_6$  (i) each is an alkyl group having 1 to 15 carbon atoms provided that  $\text{R}_1$ - $\text{R}_6$ , are not all alkyl groups, or a substituted alkyl group having 1 to 15 carbon atoms wherein the substituent is hydrogen, cyano,  $-\text{CONH}_2$ ,  $-\text{OCOCH}_3$ ,  $\text{OCOC}_2\text{H}_5$ , carbonyl, alkenyl wherein the double bond is not conjugated with the nitroxide moiety, or  $-\text{COOR}$  wherein  $\text{R}$  of the  $-\text{COOR}$  group is alkyl or aryl, or (ii) together form part of a ring having at least two carbon atoms and up to two heteroatoms of  $\text{O}$  or  $\text{N}$ ,



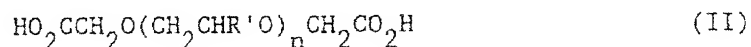
are aryl, in the presence of a  $\text{NO}_x$ -generating compound and optionally, an oxidant and/or a solvent, at a temperature in the range of

from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha ,omega-dicarboxylic acid.

The present process converts polyoxyalkylene glycols of the formula



wherein R' is hydrogen or alkyl, preferably methyl, or mixtures thereof (on the individual molecule) and n represents the average number of oxyalkylene groups and is an integer of from 0 to 5,000, preferably from 10 to 500, and more preferably 20 to 200, to the corresponding polyoxyalkylene-alpha,omega-dicarboxylic acids of the formula:



by contacting the polyoxyalkylene glycol with a stable free radical nitroxide in the presence of a NO<sub>x</sub>-generating compound and optionally, an oxidant and/or a solvent, at a temperature in the range of from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha ,omega-dicarboxylic acid.

The polyoxyalkylene glycol reactant suitably comprises one or more polyoxyalkylene glycols having a molecular weight in the range of from 100 to 250,000, preferably from 500 to 20,000, and more preferably from 1,000 to 10,000. The polyoxyalkylene glycols are typically prepared by the reaction of a glycol with an alkylene oxide in the presence of a suitable alkoxylation catalyst.

Glycols suitable for use in preparing the polyoxyalkylene glycol reactant in the present invention include ethylene glycol, diethylene glycol and triethylene glycol. In addition, glycols prepared by reacting ethylene oxide with water are also suitable for use in preparing the polyoxyalkylene glycol reactant in the present process. Specific glycols and glycol mixtures which are suitable for use in preparing the alkoxyalkanol reactant are well known and are commercially available.

The process of the instant invention is particularly suited to alkoxyated glycols. In the case of propoxylated or alkoxyated glycols, it is necessary to further ethoxylate in order to obtain oxyalkylene-alpha,omega-dicarboxylic acids. The R' groups on an

- 4 -

individual molecule can be hydrogen, methyl or mixtures thereof. For example, straight ethoxylated, straight propoxylated and mixed ethoxylated-propoxylated detergent range glycols are commercially available.

5       The term "stable free radical nitroxide" as used herein shall mean a free radical nitroxide that can be prepared by conventional chemical methods and will exist long enough to be used in a subsequent chemical reaction or examined in a static system by normal methods of spectroscopy. Generally, the stable free radical  
10       nitroxides of the present invention have a half life of at least one year. The term "stable free radical" shall also be understood to include the precursor to a stable free radical from which the stable free radical may be produced in situ.

15       The stable free radical nitroxides, as used in the present process, are precursors to catalysts, i.e., oxoammonium salts, active for the oxidation of glycols to the corresponding dicarboxylic acids. These catalysts are generated in situ by the oxidation of a stable free radical nitroxide to an oxoammonium salt with an oxygen-containing oxidant. The stable free radical nitroxide can be  
20       obtained by the oxidation of secondary amines or hydroxylamines.

The stable free radical nitroxides which are suitable for use in the instant invention have the formula:

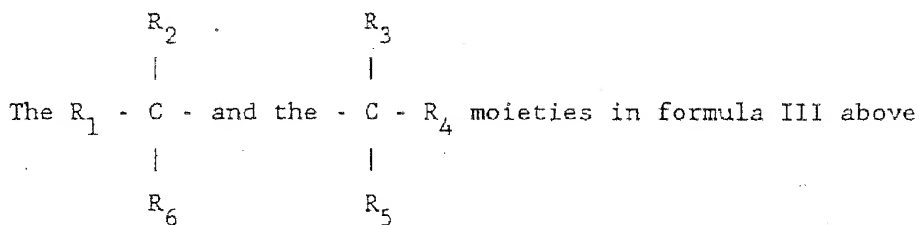


wherein each of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is an alkyl, aryl or heteroatom substituted alkyl groups and no hydrogen is bound to the remaining  
25       valences on the carbon atoms bound to the nitrogen. As used herein, the term "alkyl" is meant to include cycloalkyl. The alkyl (or heteroatom substituted) groups  $R_1$ - $R_4$  may be the same or different, and preferably contain 1 to 15 carbon atoms. Preferable,  $R_1$ - $R_4$  are methyl, ethyl, or propyl groups. In addition to hydrogen, the

- 5 -

heteroatom substituents may include, halogen, oxygen, nitrogen and the like.

The remaining valences ( $R_5$  and  $R_6$ ) in formula III above may be satisfied by any atom or group except hydrogen which can bond covalently to carbon, although some groups may reduce the stabilising power of the nitroxide and are undesirable. When  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are each alkyl groups, however, at least one of  $R_5$  and  $R_6$  must be an aryl group. Preferably,  $R_5$  and  $R_6$  are substituted alkyl groups having 1 to 15 carbon atoms wherein the substituent is selected from halogen, cyano,  $-COOR$ , wherein  $R$  is alkyl or aryl,  $-CONH_2$ ,  $-OCOC_2H_5$ , carbonyl, or alkenyl where the double bond is not conjugated with the nitroxide moiety, or alkyl groups of 1 to 15 carbon atoms.  $R_5$  and  $R_6$  together may also form a ring of at least two carbon atoms and up to two heteroatoms, such as O or N. Examples of suitable compounds having the structure above and in which  $R_5$  and  $R_6$  form part of the ring are piperidinyl-1-oxyls and pyrrolidin-1-oxyls.

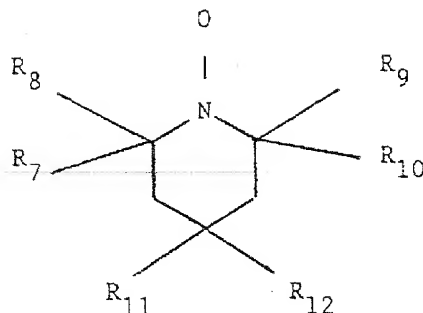


can individually be aryl, i.e., . Examples of suitable compounds

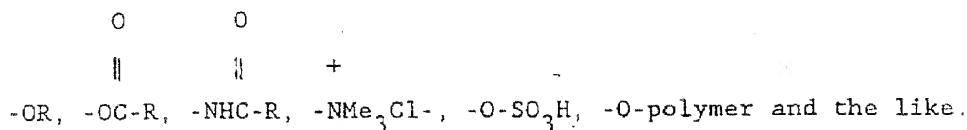
having the structure above in which the  $R_1 - C -$  and the  $- C - R_4$  moieties are individually aryl are diphenylamine, phenyl tertiary butylamine, 3-methyl-diphenylamines, 2-chlorophenylamine and the like. These compounds may be substituted with an substituents which do not interfere with the reaction.

- 6 -

In a preferred embodiment, the stable free radical nitroxide has the formula:



wherein each of  $R_7$ ,  $R_8$ ,  $R_9$  and  $R_{10}$  is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms and no hydrogen is bound to the remaining valences on the carbon atoms bound to the nitrogen, and each of  $R_{11}$  and  $R_{12}$  is alkyl, hydrogen, aryl or a substituted heteroatom. As used herein, the term "alkyl" is meant to include cycloalkyl. The alkyl (or heteroatom substituted) groups  $R_7$ - $R_{10}$  may be the same or different, and preferably contain 1 to 15 carbon atoms. Preferably,  $R_7$ - $R_{10}$  are methyl, ethyl, or propyl groups. In addition to hydrogen, the heteroatom substituents may include, halogen, oxygen, nitrogen and the like. Preferably, one of  $R_{11}$  and  $R_{12}$  is hydrogen, with the other one being a substituted heteroatom which does not interfere with the reaction. Suitable substituted heteroatoms include



In a particularly preferred embodiment, the nitroxide is selected from the group consisting of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-hydroxy-2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-pivoylamido-2,2,6,6-tetramethyl-piperidine-1-oxyl-4-sulphate, 4-alkoxy-2,2,6,6-tetramethyl-piperidine-1-oxyl, and mixtures thereof, with 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-pivoylamido-2,2,6,6-tetramethyl-piperidine-1-oxyl, and 4-alkoxy-2,2,6,6-tetramethyl-piperidine-1-oxyl being especially preferred.



- 7 -

The  $\text{NO}_x$ -generating compound in the present process is typically selected from the group consisting of an alkali metal nitrosodisulphonate, nitric acid and mixtures thereof, with nitric acid being preferred. However, any compound which serves to generate  $\text{NO}_x$  during the course of the reaction and which does not interfere with the reaction would be suitable. While not wishing to be bound by any particular theory, it is believed that nitrogen oxides ( $\text{NO}_x$ ) are generated in the reaction and are the active species in the reaction.

The alkali metal nitrosodisulphonate suitable for use as a  $\text{NO}_x$ -generating compound can be any alkali metal nitrosodisulphonate although potassium nitrosodisulphonate is preferred. As used herein, the term "alkali metal" is used as a descriptor of the elements Group IA of the Periodic Table of the Elements (Li, Na, K, Rb, Cs, Fr). The alkali metal nitrosodisulphonate is typically dissolved in water prior to being added to the reaction mixture although it can be added as a solid after all of the other reactants have been added.

As used herein, the term "nitric acid" refers to nitric acid, fuming nitric acid or nitrous acid generated by contacting a nitrate or nitrite salt such as, for example, an alkali metal salt, a tetraalkylammonium salt, an alkaline earth salt or a rare earth salt, with a strong acid such as, for example, a mineral acid. The nitric acid suitable for use as a  $\text{NO}_x$ -generating compound in the present invention typically has a concentration in the range of from 50 percent to 100 percent, preferably 70 percent. Generally, an amount of nitric acid in the range of from 5 mole percent to 1,000 mole percent, based on the moles of starting polyoxyalkylene glycol is utilised. The nitric acid is typically added to the reaction mixture after all of the other reactants have been added.

In a preferred embodiment, an oxidant is also added as a reactant. In general, when catalytic amounts of the  $\text{NO}_x$ -generating compound and nitroxide are used, the addition of an oxidant is preferred, whereas when stoichiometric amounts of the  $\text{NO}_x$ -generating compound and nitroxide are used, an oxidant may not be needed.

One skilled in the art could readily determine by routine experimentation whether or not an oxidant would be useful in the reaction. The oxidants suitable for use in the instant invention are those compounds which are capable, in the presence of a  $\text{NO}_x$ -generating compound, of oxidising the stable free radical nitroxide to the oxoammonium salt. Suitable oxidants include oxygen-containing gases such as pure oxygen and oxygen in air. Whereas pure oxygen can be preferred to accomplish the desired conversion, the oxygen can also be diluted with an inert gas such as nitrogen, helium, argon, or other similar gas. While air can be used as the oxidant, the reaction rate is much slower. For purposes of increasing the reaction rate, higher  $\text{O}_2$  pressures such as, for example, 7000 kPa (1000 psig) can be utilised. In a preferred embodiment, pure oxygen is used as the oxidant and it is bubbled into the reaction solution.

The reaction is preferably carried out in the presence of a solvent. When the molecular weight is such that the alkoxyalkanol reactant is a solid or a viscous liquid, a solvent in which the solid or highly viscous alkoxyalkanol reactant is soluble must be added. Suitable solvents are thus those in which the alkoxyalkanol reactant is soluble and those which do not interfere with the reaction. Suitable solvents include dichloromethane, triglyme, tertiary butyl alcohol, acetonitrile, carbon tetrachloride, monoglyme, diglyme, tertiary amyl alcohol and the like, and mixtures thereof. In a preferred embodiment, the solvent is selected from the group consisting of dichloromethane, acetonitrile, tertiary butyl alcohol and mixtures thereof. The weight ratio of solvent to alkoxyalkanol reactant is typically in the range of from 1:1 to 1:100, and preferably in the range of from 1:1 to 1:5.

The amounts and concentrations of the reactants utilised in the process of the instant invention can vary within wide ranges. The amount of stable free radical nitroxide is typically in the range of from 1 mole percent to 500 mole percent, preferably from 5 mole percent to 20 mole percent, based on the number of moles

starting polyoxyalkylene glycol. Generally, the amount of  $\text{NO}_x$  generating compound used is in the range of from 5 mole percent to 1000 mole percent, based on the number of moles of polyoxyalkylene glycol.

5       The process of the present invention is typically conducted under mild conditions, with good results being obtained using a temperature in the range of from 0 °C to 100 °C, preferably 20 °C to 70 °C, and most preferably, 40 °C to 60 °C. Reaction pressures are not critical although higher pressures can result in increased  
10       reaction rates. Pressures in the range of from atmospheric pressure up to about 7000 kPa (about 1000 psig) can be employed with good results.

      The process of the instant invention can be carried out either batchwise or continuously, using a stirrer equipped reactor  
15       or other well known contacting technique to achieve adequate mixing. Preferred reaction conditions, e.g., temperature, pressure, flow rates, etc., vary somewhat depending on the specific nitroxide utilised and on the concentration of the nitroxide.

      The process of the instant invention can be carried out in a  
20       variety of ways. For example, 0.0032 moles of the polyoxyalkylene glycol and 0.0064 moles of the nitroxide may be added to the reaction vessel, followed by the addition of 0.011 moles of 70 percent nitric acid. Following the reaction, the product may be separated from the reaction mixture using conventional procedures  
25       such as, for example, an extraction procedure or a precipitation procedure. The particular procedure utilised depends on whether the reaction product is a solid or liquid at room temperature. If the product is solid at room temperature, precipitation is typically used. If, however, the product is a liquid at room temperature, an  
30       extraction procedure is generally used. The reaction product can be purified by a number of conventional means such as high temperature water washing or catalytic hydrogenation.

      Depending upon process conditions and the nitroxide used, the yields of polyoxyalkylene-alpha,omega-dicarboxylic acid obtained by  
35       this invention can be greater than 98% of starting material being

- 10 -

converted. The products produced by the instant process can be used in a variety of detergent applications. For example, corrosion inhibitors, detergent builders or emulsifying agents.

5 The ranges and limitations provided in the instant specification and claims are those which are believed to particularly point out and distinctly claim the present invention. It is, however, understood that other ranges and limitations which perform substantially the same function in the same or substantially the same manner to obtain the same or substantially the same result are  
10 intended to be within the scope of the instant invention as defined by the instant specification and claims.

The process of this invention will be further described by the following embodiments which are provided for illustration and are not to be construed as limiting the invention.

15 Illustrative Embodiments

Example 1

10.9 Grams of poly(ethylene glycol) having a molecular weight of 3400, 1.0 grams of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 50 millilitres of acetonitrile and 1 gram of 70 percent nitric acid  
20 were charged to a 100 millilitre round bottomed flask. O<sub>2</sub> was bubbled through this mixture at ambient pressure. The reaction temperature was held at 35 °C over a 6-hour period. The results are presented in Table I.

Example 2

25 100 Grams of poly(ethylene glycol) having a molecular weight of 3400, 5 grams of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 200 millilitres of methylene chloride and 5 grams of 70 percent nitric acid were charged to a 500 millilitre round bottomed flask. Air was bubbled through this mixture at ambient pressure. The  
30 reaction was held at reflux over a 8-hour period. The results are presented in Table I.

Example 3

10.9 Grams of poly(ethylene glycol) having a molecular weight of 3400, 1 gram of 2,2,6,6-tetramethyl-piperidine-1-oxyl,  
35 50 millilitres of acetonitrile and 1 gram of 70 percent nitric acid

- 11 -

were charged to a 100 millilitre round bottomed flask. The reaction mixture was held open to the atmosphere. The reaction temperature was held at 35 °C over a 6-hour period. The results are presented in Table I.

5     Example 4

10.9 Grams of poly(ethylene glycol) having a molecular weight of 3400, 0.2 grams of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 50 millilitres of methylene chloride and 0.2 grams of 70 percent

10     O<sub>2</sub> was bubbled through this mixture at ambient pressure. The reaction temperature was held at 35 °C over a 5-hour period. The results are presented in Table I.

Comparative Example A

15     Comparative Example A was carried out in a manner similar to Example 1 except that no nitroxide was used. The results are presented in Table I.

Comparative Example B

20     Comparative Example B was carried out in a manner similar to Example 4 except that no nitric acid was used. The results are presented in Table I.

Comparative Example C

Comparative Example C was carried out in a manner similar to Example 4 except that no nitroxide was used. The results are presented in Table I.

25     As can be seen in Table I, nitroxide and nitric acid are necessary for the oxidation of the terminal diol to proceed.

- 12 -

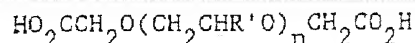
Table I

Oxidation Of Polyoxyalkylene Glycols to  
Polyoxyalkylene-Alpha-Omega Dicarboxylic Acids

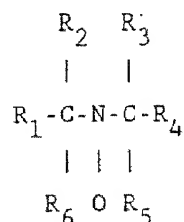
	% Conversion	% Selectivity to Dicarboxylic Acids
Example 1	>99	>99
Example 2	>99	>99
Example 3	>99	>99
Example 4	56	90
Comparative Example A	0	0
Comparative Example B	0	0
Comparative Example C	0	0

C L A I M S

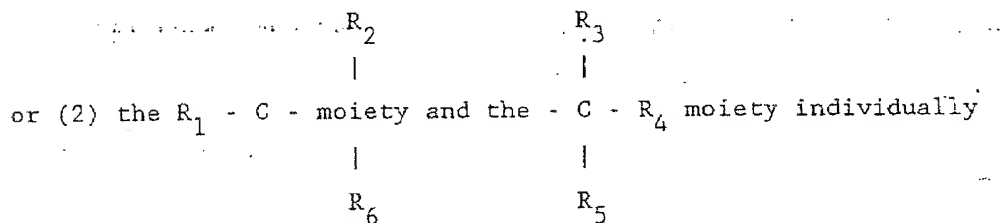
1. A process for the preparation of a polyoxyalkylene-alpha,omega-dicarboxylic acid of the formula



wherein R' is hydrogen or methyl or mixtures thereof (on the individual molecule) and n is an integer of from 0 to 5,000, which comprises reacting the corresponding polyoxyalkylene glycol with a stable free radical nitroxide having the formula:



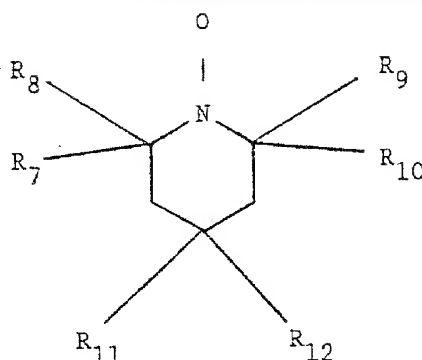
wherein (1) (a) each of R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms, and (b) R<sub>5</sub> and R<sub>6</sub> (i) each is an alkyl group having 1 to 15 carbon atoms provided that R<sub>1</sub>-R<sub>6</sub> are not all alkyl groups, or a substituted alkyl group having 1 to 15 carbon atoms wherein the substituent is hydrogen, cyano, -CONH<sub>2</sub>, -OCOCH<sub>3</sub>, OCOC<sub>2</sub>H<sub>5</sub>, carbonyl, alkenyl wherein the double bond is not conjugated with the nitroxide moiety, or -COOR wherein R of the -COOR group is alkyl or aryl, or (ii) together form part of a ring having at least two carbon atoms and up to two heteroatoms of O or N,



- 14 -

are aryl, in the presence of a  $\text{NO}_x$ -generating compound and an oxidant at a temperature in the range of from 0 °C to 100 °C and thereafter separating out the polyoxyalkylene-alpha,omega-dicarboxylic acid.

- 5 2. The process of claim 1 wherein the stable free radical nitroxide has the formula:



wherein each of  $R_7$ ,  $R_8$ ,  $R_9$  and  $R_{10}$  is an alkyl, aryl or heteroatom substituted alkyl group having 1 to 15 carbon atoms and each of  $R_{11}$  and  $R_{12}$  is alkyl, hydrogen, aryl or a substituted heteroatom.

- 10 3. The process of claim 3 wherein the stable free radical nitroxide is selected from the group consisting of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-pivoylamido-2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-alkoxy-2, 2,6,6-tetramethyl-piperidine-1-oxyl and mixtures thereof.
- 15 4. The process of any one of claims 1-3 wherein said  $\text{NO}_x$ -generating compound is nitric acid.
5. The process of any one of claims 1-4 wherein the amount of  $\text{NO}_x$ -generating compound is in the range of from 5 mole percent to 1,000 mole percent, based on the number of moles polyoxyalkylene glycol.
- 20 6. The process of any one of claims 1-5 wherein said polyoxyalkylene glycol is contacted with said stable free radical nitroxide, followed by the addition thereto of said  $\text{NO}_x$ -generating compound and said oxidant.



- 15 -

7. The process of any one of claims 1-6 wherein the amount of stable free radical nitroxide is in the range of from 1 mole percent to 500 mole percent, based on the number of moles of polyoxyalkylene glycol.

## INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/EP 93/03693A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C07C59/305 C07C51/27

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C C07B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A,5 162 579 (FRIED) 10 November 1992 cited in the application see column 2, line 28 - line 51 see claims 1-15 ----	1,4,5
Y	US,A,3 888 877 (LEHN) 10 June 1975 see column 25; example 1 see column 29; example 13A see column 42; example 47A -----	1,4,5

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

5 April 1994

Date of mailing of the international search report

14.04.94

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patendaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Klag, M

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 93/03693

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5162579	10-11-92	NONE	
US-A-3888877	10-06-75	US-A- 4156683	29-05-79
		US-A- 3966766	29-06-76
		CA-A- 1062255	11-09-79
		CH-A- 550816	28-06-74
		DE-A, C 2028556	17-12-70
		DE-C- 2066192	20-12-84
		FR-A- 2052947	16-04-71
		SE-B- 383885	05-04-76
		CH-A- 544106	28-12-73
		GB-A- 1304367	24-01-73